

Einstein's Approach to Planck's Law

In 1917 Albert Einstein wrote a remarkable paper in which he used classical statistical mechanics and elements of the old Bohr theory to derive the Planck distribution and to relate spontaneous emission, as it appears in the Bohr theory to induced emission and absorption.

We start with radiation in a cavity at temperature T . Assume that the walls of the cavity consist of atoms that can be in a variety of stationary states. These are labeled by energies E_n , and furthermore we allow for *degeneracy*—that is, the possibility that each energy level may accommodate g_n states. According to classical statistical mechanics (Boltzmann distribution), the ratio of the number of atoms in the state m to those in the state n is given by

$$\frac{N_m}{N_n} = \frac{g_m e^{-E_m/kT}}{g_n e^{-E_n/kT}} = \frac{g_m}{g_n} e^{-(E_m - E_n)/kT} \quad (1A-1)$$

Let us now consider a pair of levels of energies E_1 and E_0 with $E_1 > E_0$ (Fig. 1A-1). The number of transitions from the upper to the lower state per second—that is, the *rate* of transitions—is denoted by R_{10} . The rate of transitions from the lower to the upper level is R_{01} . The number of transitions from the lower level to the upper level must be proportional to the number of atoms in the lower state N_0 , as well as to the intensity of the radiation in the cavity. For frequency ν and temperature T this is denoted by $u(\nu, T)$. We write

$$R_{01} = N_0 u(\nu, T) B_{01} \quad (1A-2)$$

The frequency ν is the one that is absorbed in the *induced absorption*, and the constant B_{01} is called the coefficient of induced absorption.

For the transition from the upper level to the lower level, Einstein uses the Bohr postulate, according to which spontaneous emission occurs with a rate independent of the radiation present. In addition, the presence of radiation also induces transitions to the lower level. The coefficient of *induced emission* is denoted by B_{10} . If the number of atoms in the upper state is N_1 , then

$$R_{10} = N_1 (A_{10} + u(\nu, T) B_{10}) \quad (1A-3)$$

with the two terms describing spontaneous and induced emission. In equilibrium there must be as many “up” transitions as “down” transitions, so that

$$R_{10} = R_{01} \quad (1A-4)$$

It follows that

$$\frac{N_0}{N_1} = \frac{A_{10} + B_{10} u(\nu, T)}{B_{01} u(\nu, T)} = \frac{g_0}{g_1} e^{-(E_0 - E_1)/kT} \quad (1A-5)$$

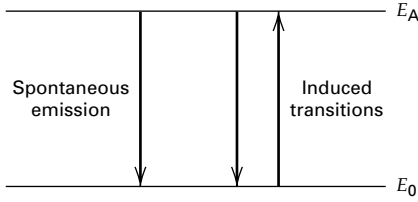


Figure 1A-1 Possible transitions in a two-level system. Downward transitions can be both spontaneous and induced by an external electromagnetic field. Upward transitions can only be stimulated.

We rewrite this in the form

$$g_1 A_{10} = u(\nu, T)(g_0 B_{01} e^{(E_1 - E_0)/kT} - g_1 B_{10}) \quad (1A-6)$$

A number of consequences can be drawn from this formula. First, in the limit of large T , for fixed $(E_1 - E_0)$,

$$e^{(E_1 - E_0)/kT} \rightarrow 1 + \frac{E_1 - E_0}{kT} + 0\left(\frac{1}{(kT)^2}\right) \quad (1A-7)$$

Furthermore, in that limit, the classical Rayleigh-Jeans formula for the energy density applies, so that

$$u(\nu, T) \rightarrow \frac{8\pi\nu^2}{c^3} kT \quad (1A-8)$$

The left side of (1A-6) is independent of T , so it follows that the term proportional to T on the right-hand side must vanish. This implies

$$g_0 B_{01} = g_1 B_{10} \quad (1A-9)$$

The meaning of this result is that the rate per atom of induced absorption is equal to the rate per atom of induced emission. The equality of the terms independent of T leads to

$$\frac{A_{10}}{B_{10}} = \frac{8\pi\nu^2}{c^3} (E_1 - E_0) \quad (1A-10)$$

If we now go back to equation (1A-6), we find that

$$u(\nu, T) = \frac{A_{10}/B_{10}}{e^{(E_1 - E_0)/kT} - 1} = \frac{8\pi\nu^2}{c^3} \frac{(E_1 - E_0)}{e^{(E_1 - E_0)/kT} - 1} \quad (1A-11)$$

The left-hand side must, on general thermodynamic grounds, obey Wien's law; that is, it must be of the form $\nu^3 f(\nu/T)$. This then has the following important consequences: $(E_1 - E_0)$ has to be proportional to ν , so that

$$E_1 - E_0 = h\nu \quad (1A-12)$$

and finally,

$$u(\nu, T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} = \left(\frac{8\pi\nu^2}{c^3}\right) h\nu \frac{1}{e^{h\nu/kT} - 1} \quad (1A-13)$$

This expression for the energy density has three components: the first one is the number of modes for the radiation field in the vicinity of ν . More precisely, we should be talking about $u(\nu, T)d\nu$; the energy density in the frequency range $(\nu, \nu + d\nu)$, and the corresponding number of modes is $(8\pi\nu^2 d\nu/c^3)$. The second factor is the energy per mode; we associate it with the energy of the quantum of radiation emitted by the decay of the upper to the lower state, because of energy conservation. Finally, the third factor is the

average number of quanta with frequency ν that make up the energy density, so that we can write

$$\langle n(\nu) \rangle = \frac{1}{e^{h\nu/kT} - 1} \quad (1A-14)$$

Let us now get back to the *emission* rate per atom. It is

$$\begin{aligned} R_{10}/N_1 &= u(\nu, T)B_{10} + A_{10} = A_{10} \left(1 + \frac{1}{e^{h\nu/kT} - 1} \right) \\ &= A_{10}(1 + \langle n(\nu) \rangle) \end{aligned} \quad (1A-15)$$

The *absorption* rate per atom is similarly found to be proportional to $\langle n(\nu) \rangle$. In *photon* language we see that both emission and absorption are enhanced by the number of photons of the right frequency that are present. Although this result was only derived for blackbody radiation, this result does not depend on the particular form of the frequency distribution.

Supplement 1-B

Estimate of the Lifetime of a Rutherford Atom

We begin with the form of $F = ma$ for a circular orbit of an electron in the Coulomb field of a proton. The equation reads

$$\frac{mv^2}{r} = m\omega^2 r = \frac{e^2}{4\pi\epsilon_0 r^2} \quad (1B-1)$$

which leads to Kepler's third law

$$\omega^2 r^3 = \frac{e^2}{4\pi\epsilon_0 m} \quad (1B-2)$$

The energy can be expressed in terms of r with the help of the above:

$$\begin{aligned} E &= \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0 r^2} r - \frac{e^2}{4\pi\epsilon_0 r} \\ &= -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 r} \end{aligned} \quad (1B-3)$$

The Larmor formula for the instantaneous power radiated—that is, the energy loss per unit time—is

$$\begin{aligned} P &= \frac{dE}{dt} = -\frac{2}{3} \frac{e^2}{4\pi\epsilon_0 c^3} \frac{a^2}{r^3} = -\frac{2}{3} \frac{e^2}{4\pi\epsilon_0 c^3} \frac{1}{r^3} \left(\frac{v^2}{r}\right)^2 = -\frac{2}{3} \frac{e^2}{4\pi\epsilon_0 c^3} \frac{1}{r^3} (\omega^2 r)^2 \\ &= -\frac{2}{3} \frac{e^2}{4\pi\epsilon_0 c^3} \frac{1}{r^4} (\omega^2 r^3)^2 = -\frac{2}{3} \frac{e^2}{4\pi\epsilon_0 c^3} \frac{1}{r^4} \left(\frac{e^2}{4\pi\epsilon_0 m}\right)^2 = -\frac{2}{3} \left(\frac{e^2}{4\pi\epsilon_0}\right)^3 \frac{1}{m^2 c^3 r^4} \end{aligned} \quad (1B-4)$$

On the other hand, it follows from the expression for the energy that

$$\frac{dE}{dt} = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r^2} \frac{dr}{dt} \quad (1B-5)$$

If we combine these equations we get

$$3r^2 \frac{dr}{dt} = -4 \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{m^2 c^3} \quad (1B-6)$$

This may be integrated, and it leads to

$$4 \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{m^2 c^3} T = [r^3(t=0) - r^3(t=T)] \quad (1B-7)$$

It simplifies matters if we write

$$\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = \left(\frac{e^2}{4\pi\epsilon_0\hbar c}\right)^2 \hbar^2 c^2 = \alpha^2 \hbar^2 c^2 \quad (1B-8)$$

We take $r(T) = 0$, and for $r(0)$ we take a number of the order of 10^{-10} m. We know from our discussion of the Bohr atom that this is approximately equal to $2a_0$ where a_0 is the Bohr radius. When we put all this together we get

$$T = \left(2\frac{\hbar}{mc\alpha}\right)^3 \frac{m^2 c}{4\alpha^2 \hbar^2} = 2\frac{\hbar}{mc^2} \frac{1}{\alpha^5} \quad (1B-9)$$

If we put in numbers we get $T = 1.3 \times 10^{-10}$ sec.